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Optimizing Signal-to-Noise Ratio of SERS Ag Capped Si Nanopillars

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Introduction

A simple approach for mass-production of wafer-scale Ag capped Si SERS nanopillars is presented. Recorded SERS spectra exhibit uniform E-field enhancement properties while retaining low background signals over large surface areas (>cm^2).

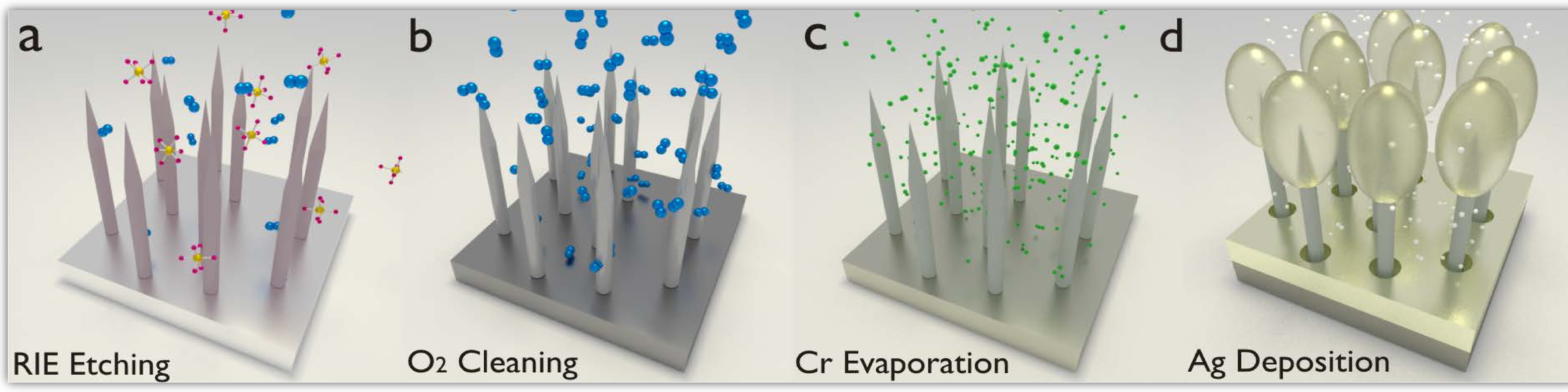

***Figure 1**. Summary of the fabrication process steps for Ag NP arrays. (a) Vertically standing Si pillars produced using maskless RIE, r ≈ 20±3 nm, h ≈ 300-1200 nm, ρNP ≈ 18±2 pillars/μm^2. (b) The Si plasma etching induced surface contaminations are removed using O_2-plasma, t = 0 – 10 min. (c) Deposition of the Cr adhesion layer to further reduce SERS background D_{Cr} = 0 – 10 nm. (d) Evaporation of Ag metal film, D_{Ag} = 100 – 300 nm.*

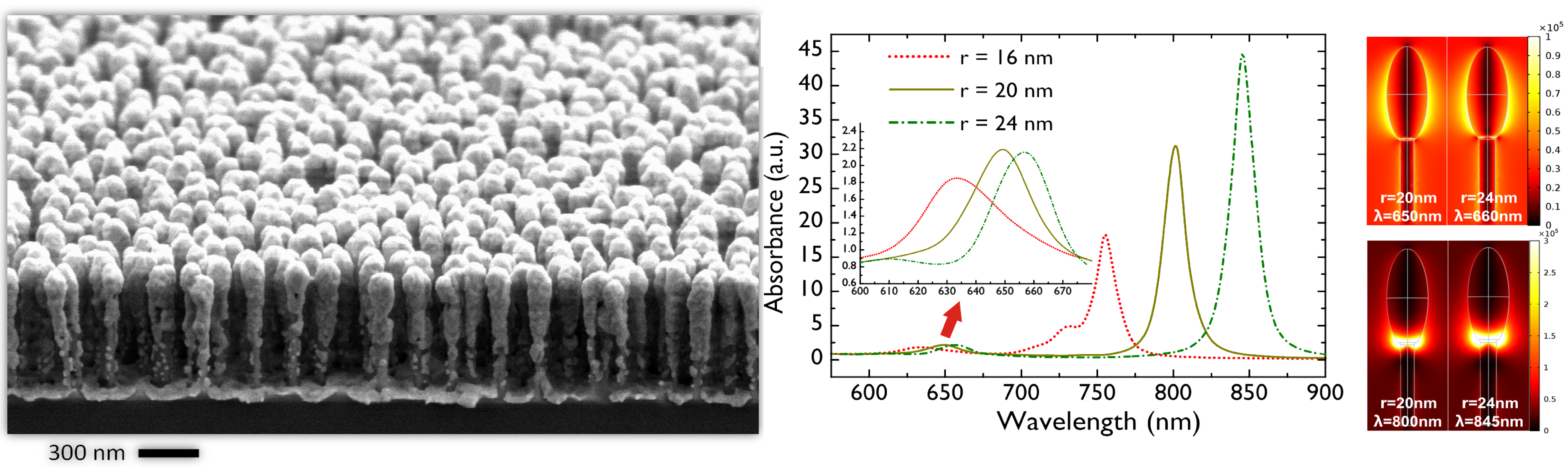

***Figure 2**. Left: SEM image of the nanopillar surface. Right: Calculated absorbance spectrum of a freestanding Si nanopillar capped by Ag. For r=20 nm and 24 nm, the corresponding field distribution is shown.*

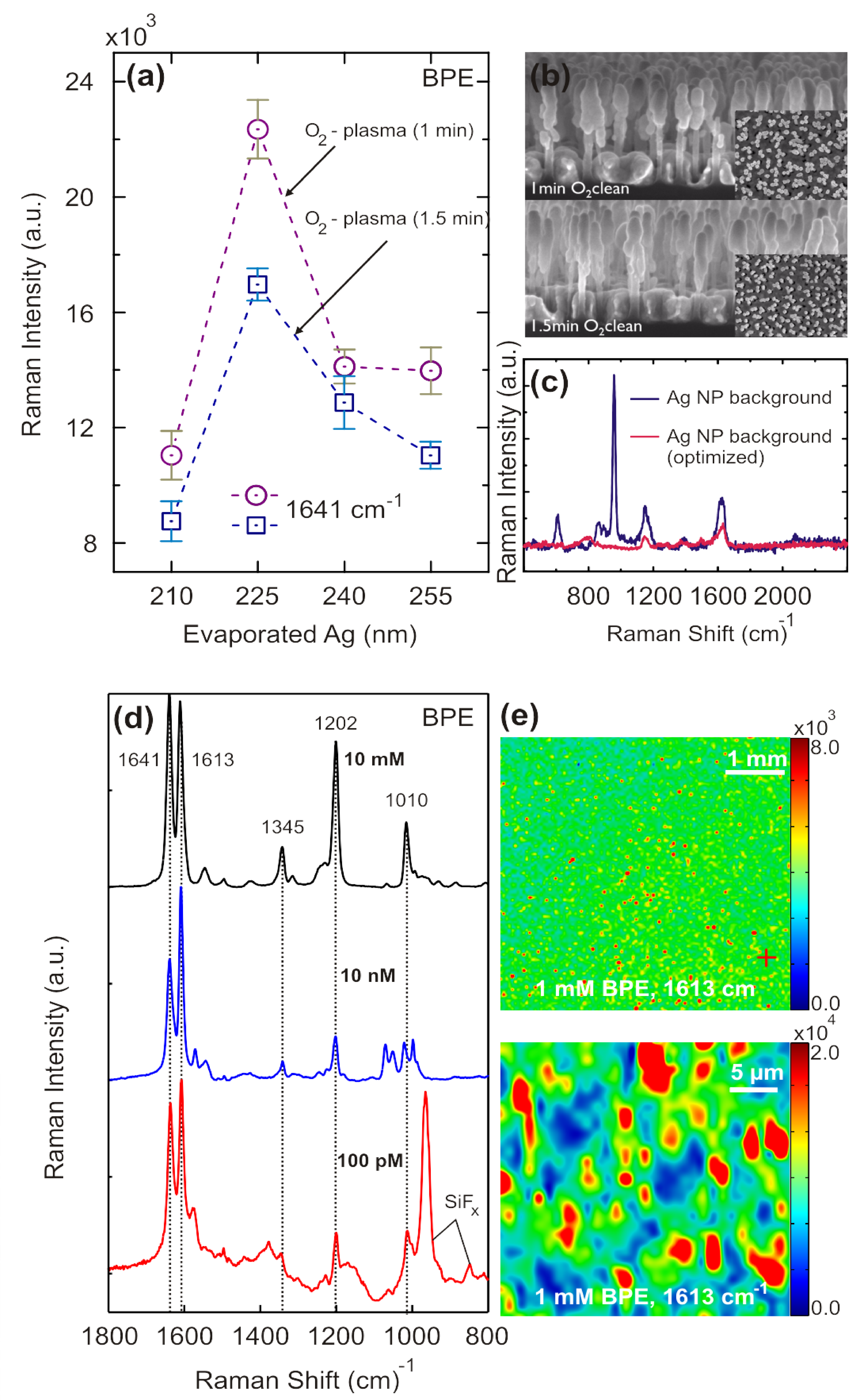

***Figure 5:** (a) Summary of SERS spectra of 10 mM BPE for substrates with varying Ag metal thickness and O_2-plasma exposure times. (b) SEM images of D_{Ag} = 225 nm Ag NP arrays exposed to 1 min (top) and 1.5 min (bottom) of O_2-plasma. Insets show the Ag NPs after exposure to 1 μL of 10 mM BPE. (c) A comparison between SERS background of standard and optimized Ag NP structures (after leaning). (d) SERS spectra of BPE recorded by optimized NPs that exhibit highest SNR. (e) Evaluation of the SERS signal uniformity using the optimized substrate.*

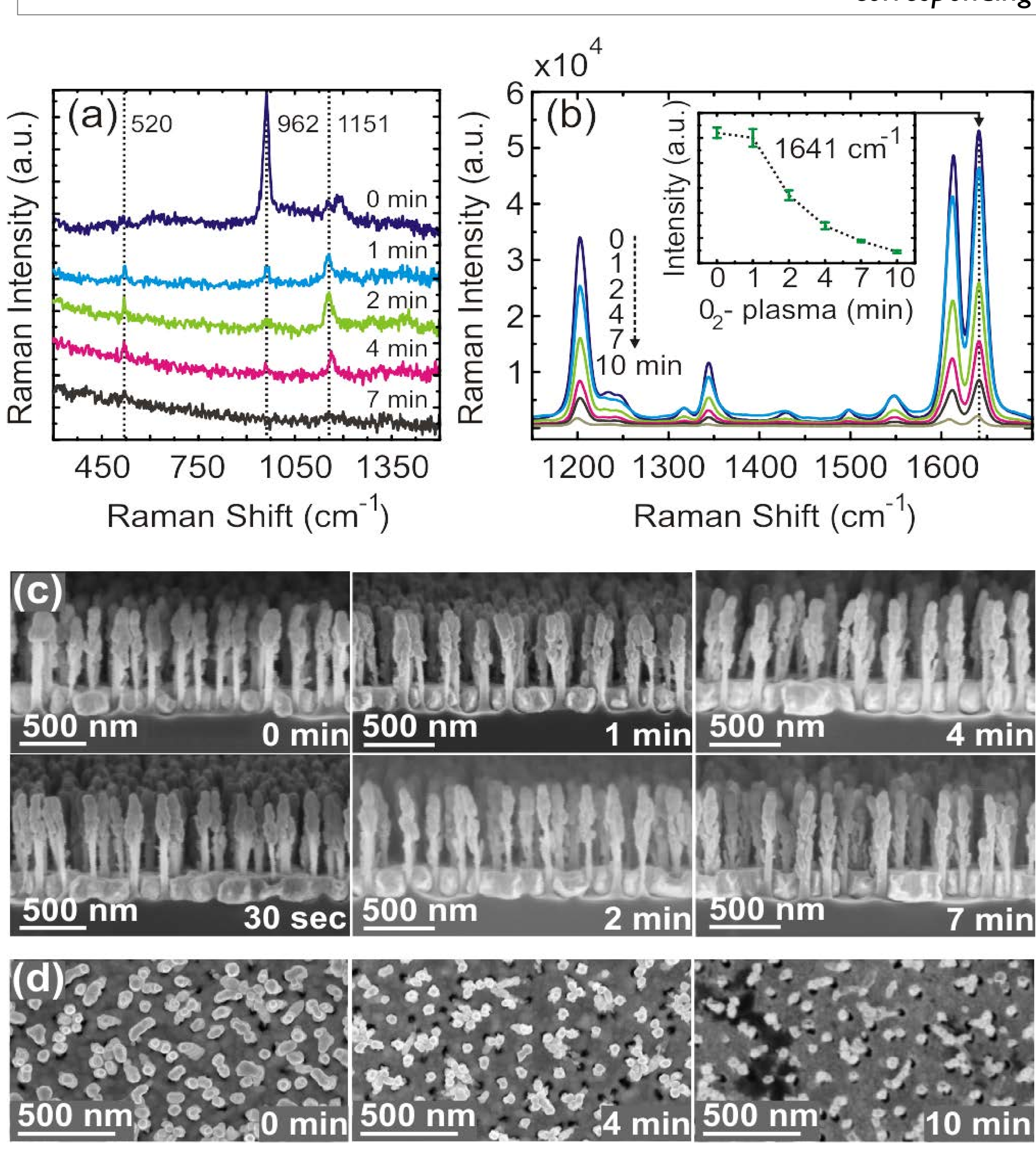

***Figure 3**. Representative SERS spectra and SEM images of the O_2-plasma treated Ag NP arrays before, (a) (c), and after, (b) (d), exposure to 1 μL of 10 mM BPE in ethanol. Solvent drying pulls Ag NPs together forming nanoclusters of varying size.*

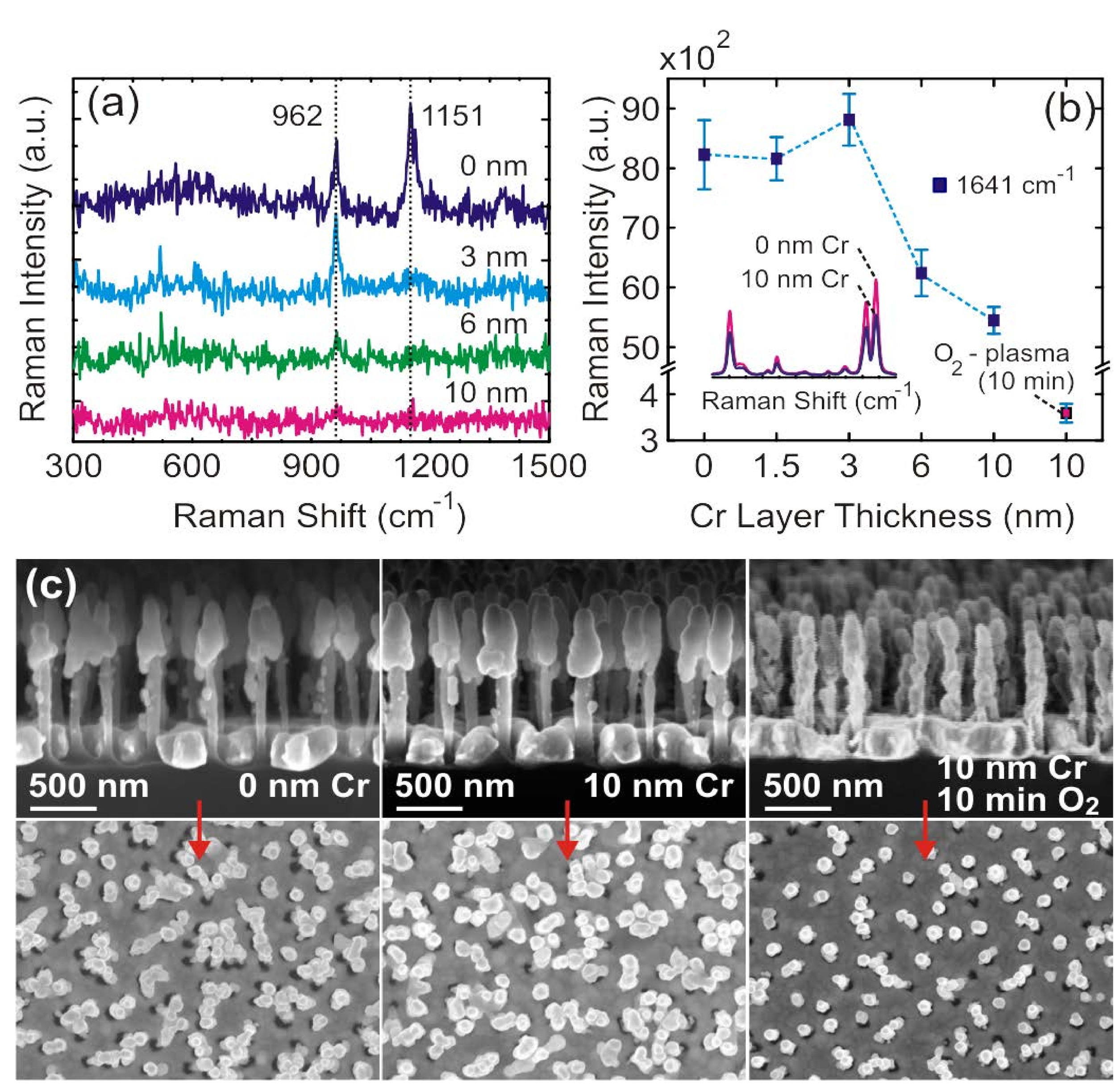

***Figure 4**. (a) Summary of SERS spectra of NP arrays for D_{Cr} = 0 – 10 nm before, (a), and after, (b), exposure to 1 μL of 10 mM BPE in ethanol. (c) Representative SEM images for D_{Cr} = 0 and 10 nm Cr adhesion layers.*

Discussion

- FEM results in figure 2 show that the most prominent resonance mode is located in the near-infrared spectral region and contributes most to the SERS performance as well as the background of Ag NPs.
- Figure 3 and 4 show that O_2-plasma exposure and Cr separation layer both reduce the background signal. However process parameters should be carefully chosen to prevent decrease of the EF. Moreover, by varying thickness of the evaporated Ag film, EFs of the SERS substrate can be further increased, see the left part of figure 5.
- Figure 5 shows that a further optimized substrate by varying thickness of Ag evaporated is able to detect 100 pM BPE showing a spectrum which contains five clear Raman vibration modes. The substrate also exhibits high EF uniformity with standard deviations of ~14% across a 5 mm x 5 mm chip.

Conclusion

A simple approach for mass-production of wafer-scale Ag capped Si SERS nanopillars is presented with emphasis on signal-to-noise ratio. Experimental findings suggest that the Ag NP substrates are strong candidates for obtaining a reliable SERS sensing at ultra-low concentrations. The fabrication process is simple, cost-effective, CMOS compatible and could be suitable for mass-production in standard IC foundries utilizing even larger Si carrier wafers.

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Reference:
[1] M. S. Schmidt, J. Hübner, A. Boisen, Large Area Fabrication of Leaning Silicon Nanopillars for Surface Enhanced Raman Spectroscopy, Advanced Materials. 2012, 24, 11.

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